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14. ABSTRACT In this program, we deposited oxide coatings of titanium and nickel by wet-chemical deposition methods, also referred to as sol-gel, which showed excellent tribological properties in previous investigations. A range of precursor solutions were synthesized and deposited onto a variety of substrates, all having excellent adhesion. Titania-rich compositions exhibited the best friction and wear properties. Microstructural analysis revealed that these coatings consisted of 50 nanometer size crystals of nickel titanate and rutile. The coefficients of sliding friction between the nickel titanate/titania coatings and several counterfaces were reduced by up to an order of magnitude, often showing no wear. The materials developed under this program extend the useful temperature limit of solid lubricants over previous technologies and will not oxidize nor become unstable in the presence of most gases or vapors. These coatings are non-toxic, easy to deposit and relatively inexpensive. The technical feasibility of these coatings is high.				
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SOL-GEL DERIVED, NANOSTRUCTURED OXIDE LUBRICANT COATINGS

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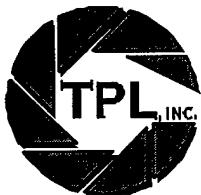
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EXECUTIVE SUMMARY

The reduction of friction and wear is essential to the proper functioning of modern machines. The more complex the machine, the more stringent the lubrication requirements. Advanced diesel engines are among the most complex of machines, and, because of their high operating speed and temperature, present one of the most challenging lubrication environments. The operating conditions for future high output diesel engines include heat loadings that will severely challenge, if not exceed, the capacity of liquid lubricants. Solid lubricants that can minimize friction and wear over the operating range of the engine are essential to minimizing the replacement cost and logistical support costs of operating advanced diesel engines. The work performed by TPL under this contract has identified oxide materials that were produced through chemical solution deposition (CSD) and provided lubrication on a variety of materials from room temperature to 600°C.

Well-developed technology exists to apply a variety of solid lubricants, molybdenum disulfide (MoS_2) being the most well known, to all sorts of metal and ceramic parts; however, these coatings require vacuum deposition techniques that are often expensive. MoS_2 is an excellent solid lubricant in dry conditions or under vacuum. In an argon atmosphere, MoS_2 will maintain a COF around 0.1 against steel until almost 800°C. On the other hand, in air, MoS_2 exhibits a COF <0.2 under similar conditions to less than 400°C, at which point the COF rises quickly to ~0.6. The change in properties is due to oxidation of the MoS_2 , which has an oxidation half life of one hour at 300°C. Since the nickel titanate developed under this program is an oxide, it will not oxidize nor will it become unstable in the presence of most gases or vapors.

This program sought to develop tribological coatings with good friction and wear behavior, which are economical and able to be applied to many surfaces, while at the same time being durable and resistant to an oxidizing atmosphere. Previous research had shown titanium oxide coatings containing significant quantities of nickel provided lubricious surfaces without the need for liquid lubrication. The strategy used here was to employ sol-gel processing to deposit coatings with tailored compositions and microstructures that would produce the desired properties and make them easy to apply and relatively inexpensive. By depositing stoichiometric amounts of titanium oxide and nickel oxide, nickel titanate was formed after firing the coatings to 800°C.

Nickel titanate coatings were applied to both Hastalloy and silicon substrates by spin- and dip-coating. The program investigated single- and multi-layer films. Friction and wear was tested using rotating and reciprocating pin-on-disk testers. The lowest coefficients of friction (COFs) were achieved with titania-rich coatings, which were characterized by a microstructure of roughly 50 nm nickel titanate and rutile (TiO_2) crystallites. Several samples obtained COFs near or below 0.1 against a TiC counterface (1 N force, 2 cm/s). Others exhibited steady performance with COFs near or below 0.2 against TiC or 52100 steel pins (1 N, 2 cm/s). This represents a significant decrease in COF from the value of TiC against Hastalloy (*i.e.*, 0.9) or steel against steel (~0.6). Testing was also performed under different environments: vacuum, nitrogen, and high humidity. Silicon nitride and 52100 steel produced COFs around 0.3 and 0.1, respectively, against nickel titanate coatings in a dry environment (vacuum or nitrogen). Titanium carbide yielded a COF of 0.15 against nickel titanate in the humid atmosphere. These results show that coatings for tribology is not a one solution fits all problem, but solutions must be designed according to the materials and atmospheres involved.

Following friction testing, the ball (or pin) and plate (disk) were examined for wear by optical microscopy, optical profilometry, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and Auger microscopy. Optical microscopy showed that many coatings were barely scratched after the one hour friction/wear test. The optical profilometer provided quantitative information on wear track depth, which allowed calculation of wear rates. SEM also provided analysis of the surface morphology, as well as compositional information near the surface of the coupons through EDS. Auger microscopy revealed the composition of transfer films, either from the pin to the disk or through mechanical mixing at the surface.

All technical objectives were met. A stable, titania-rich nickel titanate coating was developed that can be applied to metal or ceramic surfaces and significantly reduced the coefficient of friction and wear of these surfaces under given conditions. The coating can be cured at low enough temperatures for it to be applicable to most aerospace alloys and ceramics. The coating process is economical and can be readily scaled-up for large and complex parts. Several applications for this technology include low friction coatings for bearings, journals, and other wear-intensive parts; gun barrel coatings; and coatings for down-hole drilling shafts.

2. PHASE II TECHNICAL OBJECTIVES

A number of studies have shown that the introduction of lubricious solid films, especially metal oxides, can improve elevated temperature tribological performance. Two such studies have identified a class of oxides that offer exceptional tribological performance at elevated temperatures. Certain combinations of ion-implanted titanium and nickel yielded coefficients of friction (COF) of 0.06 - 0.09 at 800°C. Examination of the surface layers by Auger spectroscopy indicated that the low friction coefficients were obtained on surfaces with a titanium oxide film that had substantial nickel content. The second study demonstrated dramatic reduction in the wear of silicon nitride by adding 15 volume percent titanium carbide. Reductions in the COF by up to 50% were also obtained. Auger spectroscopy of the wear tracks identified a mixed titanium and silicon oxide as the lubricious species in the titanium carbide-containing silicon nitride.

In Phase I, we developed wet chemical methods of depositing the titanium oxide materials believed to be responsible for the improved tribological performance observed in previous studies. We hypothesized that deposition of the oxides as nanostructured materials would promote lubricious behavior at sub-ambient temperatures. The research started under Phase I was continued and further developed under a Phase II contract. Microstructure was examined by X-ray diffraction (XRD) of powders, energy dispersive spectroscopy (EDS) in a scanning electron microscope (SEM), and thermal analysis (TGA/DSC). COF was measured by reciprocating ball-on-plate at 25°C and 500°C. Wear tracks were observed with surface profilometry, optical microscopy and SEM. Titania/nickel oxide coatings reduced the COF by at least 50% at both temperatures and demonstrated the best wear resistance.

The goal of the Phase II program was to develop a range of sol-gel derived coatings for use as solid lubricants over a wide temperature range. These coatings were to reduce friction and wear in engine and bearing applications for the U.S. Air Force and commercial applications. The sol-gel approach facilitated the application of a wide variety of ceramic coatings to most substrate materials or geometries. Several compositions were investigated. The Phase II effort was directed toward developing sol-gel derived tribological coatings and characterizing them for friction/wear applications. In this final technical report, we present results obtained during the Phase II program with respect to microstructure and processing parameters.

3. WORK PERFORMED

In the first half of the Phase II effort, we determined that titania-rich nickel titanate compositions yielded the best tribological performance in the TiO₂-NiO system. The microstructure of these compositions was characterized by nickel titanate crystals and rutile, both nominally 50 nm in diameter. We showed that we could successfully coat a variety of materials with sol-gel derived nickel titanate compositions. The friction of titanium carbide (TiC) pins and 52100 stainless steel pins on coated Hastalloy coupons was reduced by up to an order of magnitude and showed little or no wear.

Precursors to the various nickel titanate coatings were synthesized using wet chemistry. Nickel (II) acetate tetrahydrate was first dissolved in distilled ethanol and concentrated nitric acid. After stirring for several hours, titanium (IV) isopropoxide was added drop wise to the stirring solution. The amounts of the starting materials depended upon the desired composition. The reagents were allowed to react for several more hours before the precursor solutions were used for coating. Films were deposited by dipping or spinning depending on the geometry of the substrate. Fresh coatings were usually dried at 100°C for 15-30 minutes and then fired at the final temperature, which was typically 800°C.

X-ray diffraction was performed by drying the various precursor solutions to form powders, which were much more amenable to analysis. The solutions were usually dried in a watch glass, initially at ambient, and then at moderate temperatures (*i.e.*, 100°-200°C) for many hours. Final firing was performed in alumina crucibles to the desired temperature. The XRD measurements were performed at Southwest Research Institute (SwRI) under their subcontract.

Friction and wear tests were performed at SwRI using a reciprocating wear tester in an environmental chamber to control the ambient conditions (*i.e.*, humidity, atmosphere). Most tests ran for one hour (3600 cycles) with a 1 N load and 1 cm stroke. Details of the wear tester can be found in the *Journal of Materials Science* 23 (1988) pages 946-957. A few friction/wear tests were run at Wright Laboratories, Dayton, Ohio (courtesy of Dr. J.S. Zabiniski). The details of these tests are given in the text with the results.

Monoliths of nickel titanate were fabricated to obtain physical properties of the bulk material. Nickel titanate pellets were made by first mixing stoichiometric amounts of nickel and titania powders. The powders were ball milled and then calcined at 1000°C for 48 hours. Each pellet was formed by uniaxially pressing the calcined powders at 70 MPa (10,000 psi) for one minute. The green pellets were placed on alumina plates and covered with an alumina crucible before being placed into a cold furnace. They were heated at 5°C/min to 900°C and then 12°C/min to 1300°C, where they were allowed to soak for 10 hours. The cooling rate was 5°C/min. The crystallinity of the calcined powders (before pellet formation) was determined by XRD (SwRI). Density of the final pellets was measured by the Archimedes method in our laboratory. Refractive index (at 632.8 nm) of the monoliths was determined using ellipsometry on a polished sections. Coefficient of thermal expansion (CTE) was measured by dilatometry at New Mexico Tech (Socorro, New Mexico). Vickers Hardness measurements were also performed at New Mexico Tech.

4. RESULTS

Spectroscopy

X-ray diffraction spectra showed the crystalline phases present in each composition. Crystallite size was calculated from the diffraction peaks using the Sherrer formula.¹ These results, covering the initial range of compositions, are listed in Table I and show that the oxide compositions produced in this work are nano-structured. Crystallite sizes ranged from roughly 6 nm to 75 nm at this heat treatment. Since the TiO₂-NiO materials possessed the best friction/wear behavior, other compositions of this binary system were investigated. Crystallization data for the TiO₂-NiO system are given in Table II. Only titania and nickel oxide combined to form a mixed metal oxide phase, nickel titanate in this case (NiTiO₃). Figure 1 displays an XRD spectrum for 75 wt.% TiO₂ - 25 wt.% NiO showing the formation of nickel titanate. Crystallite sizes for TiO₂, NiO and NiTiO₃ were consistently between 40 nm and 50 nm. Experiments were performed to determine if crystal growth would be problematic at higher temperatures or over longer periods of time at high temperatures. Nickel titanate crystallites were virtually the same size after firing to 800°, 1000°, 1200° or 1400°C for one hour, or at 800°C for 8 hours.

Infrared spectroscopy confirmed intimate mixing of the metal ions by the presence of Ti-O-Ni bonds. On the other hand, for example, Si-O-Ni bonds were not evident in the silica/nickel oxide composition, nor did mixed oxide phases develop; only NiO crystalline peaks were detected. Crystallization of NiO into Bunsenite occurred at roughly 540°C, according to DSC. Thermal analysis alone was unable to determine the crystallization temperatures for all of the other phases without more rigorous XRD experiments.

Table I: Microstructure of Wet-Chemically Derived Oxides

COMPOSITION (in weight percent)	PHASE(S)	CRYSTALLITE SIZE (nm)
50% TiO ₂ - 50% SiO ₂	amorphous	n/a
50% SiO ₂ - 50% NiO	NiO	17
50% TiO ₂ - 50% NiO	NiTiO ₃	47
	TiO ₂ (rutile)	47
	NiO	51
67% TiO ₂ - 33% SiO ₂	TiO ₂ (anatase)	6.3
	TiO ₂ (rutile)	trace
33%TiO ₂ -33%SiO ₂ -33%NiO	NiO	33
	Ni ₃ TiO ₅	trace
	TiO ₂ (rutile)	7.6
50%TiO ₂ -25%SiO ₂ -25%NiO	NiTiO ₃	18
	TiO ₂ (anatase)	8.2
	TiO ₂ (rutile)	11
	NiO	28

¹B.D. Cullity, Elements of X-Ray Diffraction, second edition, Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1978, p. 102.

Table II: Crystallinity of Wet-Chemically Derived Nickel Titanates

COMPOSITION (in weight percent)	PHASE(S)	CRYSTALLITE SIZE (nm)
25% TiO ₂ - 75% NiO	NiTiO ₃	44
	NiO	44
33% TiO ₂ - 67% NiO	NiTiO ₃	49
	NiO	45
50% TiO ₂ - 50% NiO	NiTiO ₃	47
	TiO ₂ (rutile)	47
	NiO	51
67% TiO ₂ - 33% NiO	NiTiO ₃	42
	TiO ₂ (rutile)	40
	NiO	48
75% TiO ₂ - 25% NiO	NiTiO ₃	48
	TiO ₂ (rutile)	44

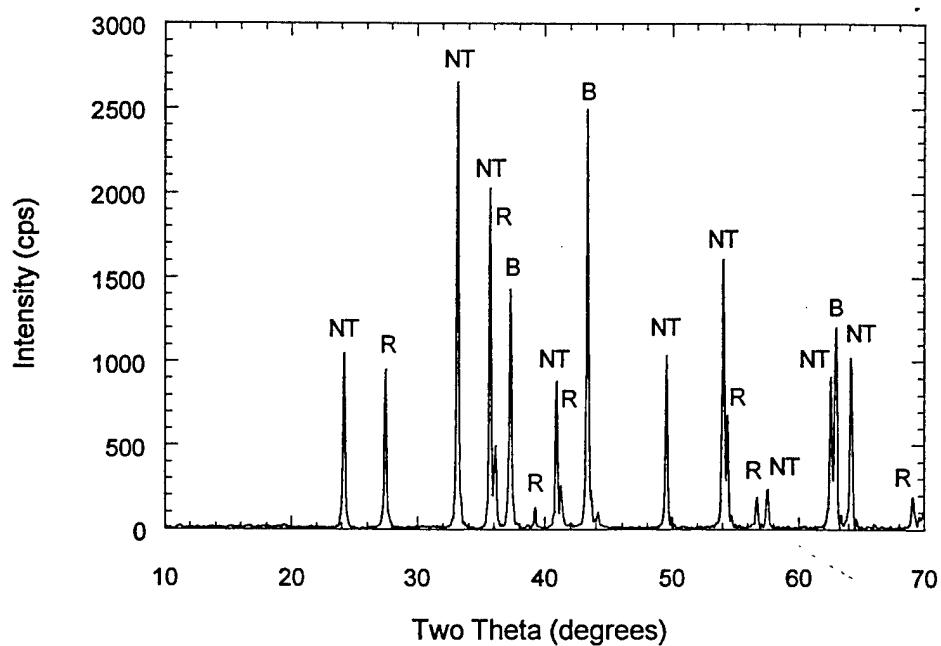


Figure 1. X-ray diffraction spectrum of 50 wt.% TiO₂-NiO made by sol-gel methods. NT = nickel titanate (NiTiO₃), R = Rutile (TiO₂), B = Bunsenite (NiO)

Tribology

Coefficient of friction values ranged from 0.08 to roughly 0.9, which appeared to be the value of the TiC pin on bare Hastalloy. Figures 2 and 3 show COF as a function of time in the friction tester at room temperature and at 500°C, respectively. From the graphs, the material with the best performance at both temperatures was the titania-rich $\text{TiO}_2\text{-NiO}$ composition. The 67 wt.% (weight percent) TiO_2 and 75 wt.% TiO_2 (not shown) compositions (balance nickel) had similar performance, and both had lower COFs than the 50 wt.% composition. Nickel-rich compositions (not shown) had COFs between the titania-rich compositions and the 50 wt.% composition. All of the $\text{TiO}_2\text{-NiO}$ compositions and the 33 wt.% ternary composition had excellent wear resistance; specifically, no wear tracks were evident after one hour, or 3600 cycles, of testing. On the other hand, the $\text{SiO}_2\text{-TiO}_2$ compositions and the $\text{SiO}_2\text{-NiO}$ composition had high wear rates.

Just for comparison, we made and tested 100% rutile films. The steady state COF between the rutile coatings and TiC pins was 0.20 at room temperature and 0.55 at 500°C. All of the other test conditions were similar to those for the samples discussed above.

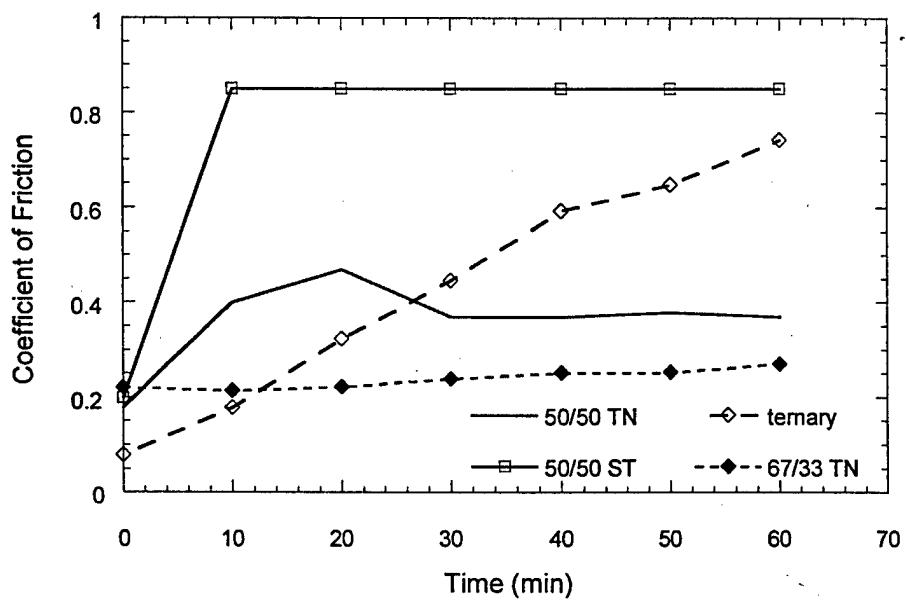


Figure 2. Sliding coefficient between wet-chemically derived oxide coatings on Hastalloy and a TiC pin as a function of time. Test conditions: room temperature, in air, 1 N load, 2 cm/s, and 1 Hz oscillation frequency. The binary compositions are listed by weight percent, where TN is $\text{TiO}_2\text{/NiO}$ and ST is $\text{SiO}_2\text{/TiO}_2$, and the ternary is 33 wt.% each of TiO_2 , SiO_2 and NiO.

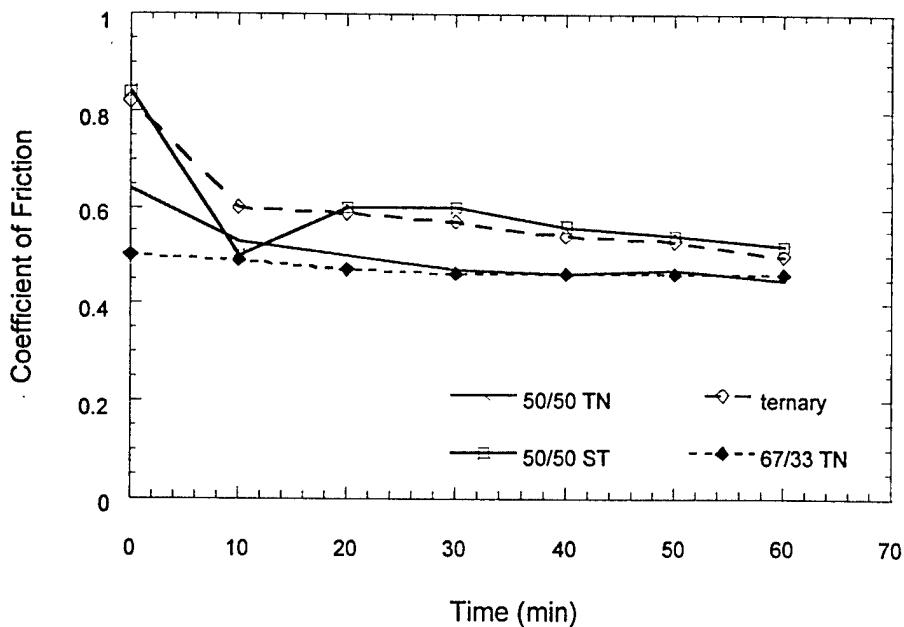


Figure 3. Sliding coefficient between wet-chemically derived oxide coatings on Hastalloy and a TiC pin as a function of time. Test conditions: 500°C, in air, 1 N load, 2 cm/s, and 1 Hz oscillation frequency. The binary compositions re listed by weight percent, where TN is TiO_2/NiO and ST is $\text{SiO}_2/\text{TiO}_2$, and the ternary is 33 wt.% each of TiO_2 , SiO_2 and NiO .

Further testing was performed on the titania-rich nickel titanate composition to determine the conditions under which it worked best. Three atmospheres and three counterface materials were chosen for the test matrix. Friction and wear tests were conducted under vacuum, nitrogen (dry), and humid air (~70% relative humidity). The friction pairs consisted of 75 wt.% TiO_2 – 25% NiO coatings on Hastalloy X and TiC, Si_3N_4 , and 52100 steel pins. Figures 4 and 5 show the COF results in nitrogen and humid air, respectively. The lack of water and oxygen appeared to favor a low COF with steel as the counterface (Figure 4). On the other hand, the moist atmosphere gave the TiC pins good lubricity against the nickel titanate coating and impeded lubricity for the steel pins (Figure 5). These data emphasized the point that tribological coatings act differently depending on the friction pair and atmosphere—it is not a one coating fits all game. The dry atmosphere data confirmed the increase in COF with temperature (*i.e.*, 500°C, Figure 3) with the TiC pins because there was little to no water available at that temperature.

Under all circumstances (vacuum, nitrogen, humid air, and high temperature), silicon nitride had a high COF against nickel titanate coatings. The COF values with the silicon nitride pins ranged from 0.30 to 0.94. The only exception to the high COFs for silicon nitride was under a room-temperature dry environment (*i.e.*, vacuum, nitrogen) against stoichiometric nickel titanate. Since we determined earlier that titania-rich coatings were the best performers, no other data were taken to examine this behavior.

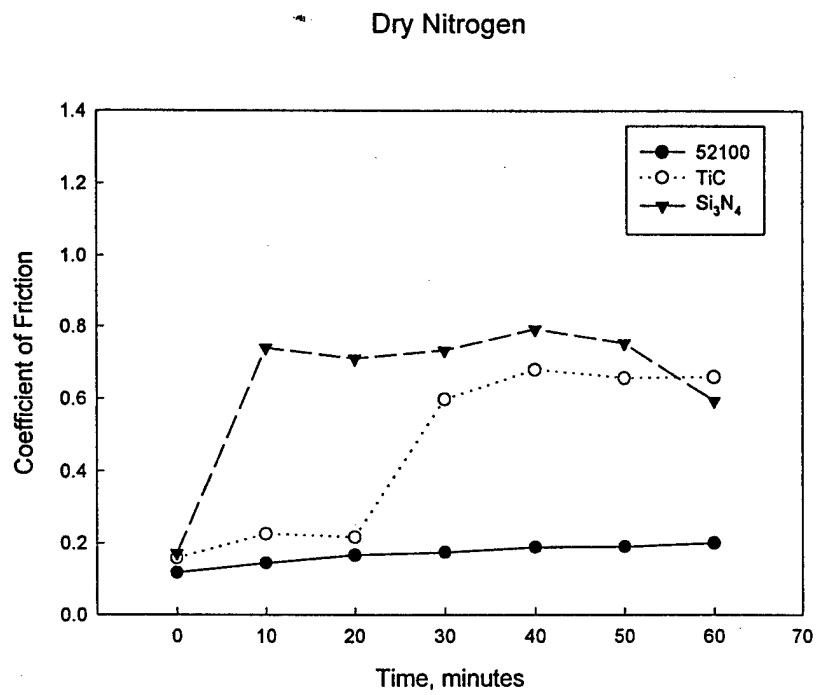


Figure 4: COF between titania-rich nickel titanate films and the stated materials under dry nitrogen.

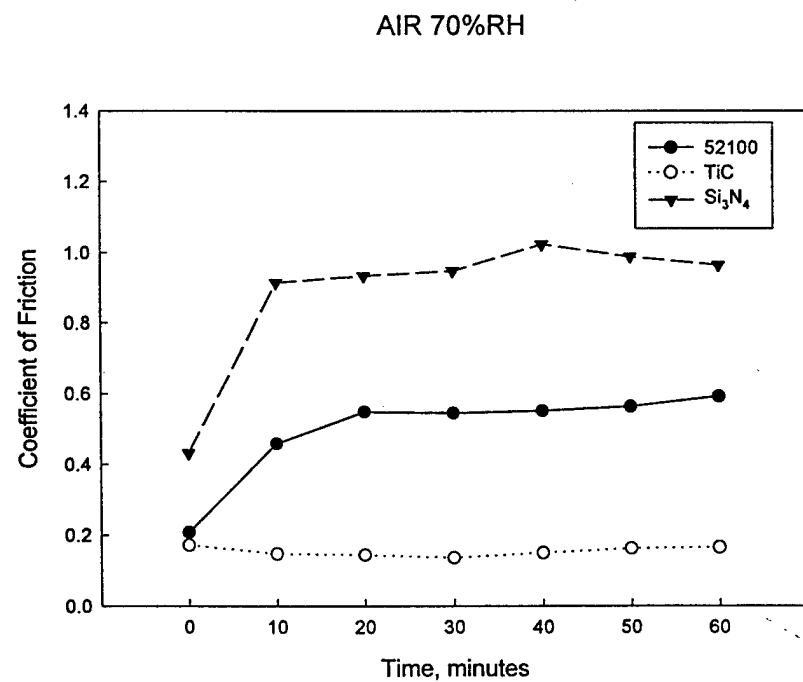


Figure 5: COF between titania-rich nickel titanate films and the stated materials in humidity.

The COFs between nickel titanate coatings and silicon nitride pins are summarized in Table III. Two compositions were used in these tests: one that was rich in titania and the other that was nearly stoichiometric, based on the metal ions. The original composition of the former was 75 wt.% TiO₂ – 25 wt.% NiO. When all of the NiO was used to form nickel titanate, the final composition was roughly 51 wt.% nickel titanate and 49 wt.% rutile (TiO₂). The composition labeled stoichiometric is actually 50 wt.% of TiO₂ and NiO, which is slightly rich in NiO (48.3 mol% TiO₂ - 51.7 mol% NiO). As determined by XRD, this composition is primarily nickel titanate with lesser amounts of rutile and bunsenite (NiO). The measurements marked with an asterisk were made at SwRI using the reciprocating friction tester used throughout this contract. The other data in Table III were obtained by Ben Phillips in Dr. J.S. Zabinski's laboratory. They were run for 10,000 cycles with a 100 g load (0.1 N) and the atmospheric conditions listed in Table III. In general, friction coefficients were high between nickel titanate and silicon nitride.

Table III: COF under various conditions using Si₃N₄ pins

Sample	Main Condition	Coefficient of Friction	Standard Deviation
Ti-rich NT	Ambient*	0.93	0.004
Ti-rich NT	Vacuum	0.81	0.13
Ti-rich NT	Nitrogen	0.65	0.10
Ti-rich NT	Humidity	0.87	0.13
Ti-rich NT	600°C	0.43	0.03
Stoichiometric NT	Ambient*	0.94	0.02
Stoichiometric NT	Vacuum	0.31	0.09
Stoichiometric NT	Nitrogen	0.30	0.05
Stoichiometric NT	Humidity	0.68	0.08
Stoichiometric NT	600°C	0.50	0.02

Ti-rich NT = 75 wt% TiO₂ – 25 wt% NiO

Stoichiometric NT = 50 wt% TiO₂ – 50 wt% NiO

Optical profilometry, SEM, EDS, and Auger spectroscopy were employed to evaluate wear tracks that resulted after 3600 cycles on the friction tester. (No post-wear evaluations were performed on the samples tested in Dr. Zabiniski's laboratory.) Wear scars varied from tracks with no discernable depth to tracks that were deeper than the thickness of the coating, which indicated complete coating removal during wear/friction testing. To confirm the presence or absence of a coating, surface composition was measured by EDS in the SEM. For TiO₂-NiO coatings, the spectra were identical inside and outside of the wear track. Nickel, titanium, oxygen, molybdenum and chromium were found inside and outside of the wear tracks. The Hastalloy X substrate contained 49% Ni, 22% Cr, 20% Fe and 9% Mo. These elements were detected with EDS because the depth of the sampling volume (~1 μm) was greater than the thickness of the coating. Since nickel was common to both coating and substrate, it was the strong presence of titanium and oxygen that indicated the coating material was present in the wear track. Concerning the counterfaces, optical microscopy showed little wear on the TiC pins. However, in experiments using Si₃N₄ pins (at SwRI), significant wear was observed on the pins, while there was little to no wear on the nickel titanate coated substrates. As mentioned earlier, COFs were much higher in the friction tests with Si₃N₄ pins than those using TiC pins, despite the lack of coating wear. In the tests with TiC pins, the COF increased to 0.8 - 0.9 only when the

coating had been worn through. This was not the case with Si_3N_4 pins. However, since COFs did not show significant promise with silicon nitride as the counterface, further analysis was not determined to be a good use of contract resources.

Auger spectroscopy was extremely useful in examining wear tracks and counterfaces because it gathered chemical information from only the top few atomic layers of the samples. Auger depth profiling was performed on the two best low friction pairs: TiC pin in moist atmosphere and 52100 pin in nitrogen. The only elements found on the TiC pin were Ti, C and O. Since the test was performed in a humid environment, it would have been easy for a small amount of the titanium to oxidize. With no nickel present, it was unlikely that any of the film transferred to the pin. Likewise, analysis of the plate showed no significant evidence of TiC transferring to the film. The elements found in the film were Ti, C, O, and Ni. Although carbon was present, it was to a lesser degree than what was found in the wear track made by the steel pin, which contained less carbon than the TiC pin. Titanium oxide appeared to be the dominant species at the surface of the film. This was expected due to the starting composition (*i.e.*, 75 wt.% TiO_2).

The surface layers were easier to track for the steel/nickel titanate pair because the only source of Fe was the pin and the only source of Ti was the film. The steel pin showed evidence of N and O, but no Ti or Ni, which indicates no transfer of the film to the pin. Since friction/wear testing was performed under nitrogen, it is likely that some kind of an iron oxynitride formed. The amount of oxygen decreased with depth faster than did nitrogen. On the other hand, iron was found in the film even after 30 sec of sputtering (roughly 20 nm). Nitrogen was also present in the upper most layers of the film. After a minute of sputtering (roughly 40 nm deep), only Ti, Ni, O, and a trace amount of C were found in the film. Therefore, only a small amount of the steel pin was transferred to the nickel titanate film.

Ellipsometry

Ellipsometry was employed to determine thickness and index of refraction of the coatings. Individual layer thickness depended upon each precursor solution and the deposition conditions. When thickness was below 0.5 micron, multiple layers were deposited to achieve coatings that were at least this thick. Refractive index (RI) varied with composition. For example, RI of the 50 wt.% SiO_2 - TiO_2 composition was measured to be 1.75, which indicated 6% porosity based on the theoretical RI for this composition. Porosity was calculated using literature values and the Maxwell Garnett effective medium approximation model. This model assumes spherical inclusions (pores in this case) and dipole interactions, which are standard first approximations that give reasonably accurate results.²

The index of refraction of monolithic nickel titanate was measured from the pressed pellets to be 2.31. Since the pellets were 92% dense (4.7 g/cc from the Archimedes method and 5.1 g/cc x-ray density), the refractive index for dense nickel titanate is 2.42. Using this experimentally determined value allowed us to calculate general porosity figures for the deposited films. For example, the 75 wt.% TiO_2 - 25 wt.% NiO precursor solution produced coatings that were roughly 51% nickel titanate and 49% rutile. The calculated refractive index for this composition was 2.5 using a first-order rule of mixtures. After firing to 800°C, this composition routinely had a measured refractive index of 2.1. Employing the Maxwell Garnett

²H.G. Tompkins, A User's Guide to Ellipsometry, Academic Press, San Diego, 1993.

effective medium approximation, we estimated that the porosity of the film was 27%. This seems rather high for films that were fired to 800°C, but the XRD show what phases are present and roughly to what extent.

Miscellaneous Data

Monoliths of nickel titanate were pressed and fired from mixed and calcined powders made in our lab. We made these pellets to measure properties that were not readily available in the literature. By evaluating the 92% dense monoliths, we found the refractive index to be 2.31 at 632.8 nm, the hardness to be 940 HV (300 g load, 20 s), and the CTE to be 7.9 ppm at 100°C, 9.7 ppm at 600°C and 10.3 ppm at 1000°C.

5. CONCLUSION: ESTIMATE OF TECHNICAL FEASIBILITY

Nanostructured solid oxide lubricants in the nickel titanate-titania system significantly reduce friction and wear in certain test systems. Coefficients of sliding friction between 52100 stainless steel or titanium carbide and nickel titanate coatings were observed as low as 0.1. The former performed best under a dry atmosphere, while the latter performed best under humid conditions. Since the lack of atmospheric water appears to enable low friction and wear against a steel counterface, these properties should be maintained at elevated temperatures. On the other hand, titanium carbide exhibited good tribological performance at elevated temperatures, where there is little moisture. Therefore, it is feasible to make nanostructured oxide lubricant coatings by sol-gel methods that operate over a wide temperature range.

It may sound as if these materials systems are limited in their applications; however, all solid lubricant, including the most well known and studied, are effective only under certain conditions. For example, MoS₂ is an excellent solid lubricant in dry conditions or under vacuum. In an argon atmosphere, MoS₂ will maintain a COF around 0.1 against steel until almost 800°C. On the other hand, in air, MoS₂ exhibits a COF <0.2 under similar conditions to less than 400°C, at which point the COF rises quickly to ~0.6. The change in properties is due to oxidation of the MoS₂, which has an oxidation half life of one hour at 300°C. The solid lubricants developed and studied under this program extend this temperature limit by several hundred degrees and will not oxidize nor become unstable in the presence of most gases or vapors. Furthermore, the NSO coatings are non-toxic, easy to deposit and relatively inexpensive. The technical feasibility of extending sol-gel derived nickel titanate coatings to real world applications is high.

6. PERSONNEL SUPPORTED

- 6.1 Douglas J. Taylor, Ph.D. - Principal Investigator
- 6.2 Stuart T. Schwab, Ph.D. - Project Manager (through November 1999)
- 6.3 Patrick F. Fleig - Staff Scientist (through November 1999)
- 6.4 Richard A. Page, Ph.D. - Associate Investigator (under SwRI subcontract)

7. PUBLICATIONS

D.J. Taylor, P.F. Fleig, S.T. Schwab and R.A. Page, "Sol-Gel Derived, Nanostructured Oxide Lubricant Coatings," *Surface and Coating Technology* 120-121 (1999) 465.

D.J. Taylor, P.F. Fleig and R.A. Page, "Sol-Gel Derived Nickel Titanate for Tribological Coatings," in *Sol-Gel Commercialization and Applications*, Proceedings of the 102nd Annual Meeting of the American Ceramic Society (2000).

D.J. Taylor and D.P. Birnie III, "Striation Reduction in Spin-Coated Films: Sol-Gel Derived Aluminum Titanate Case Study," *Thin Solid Films*, in press (2000).

7. INTERACTIONS

A presentation entitled "Sol-Gel Derived, Nanostructured Oxide Lubricant Coatings" was delivered by Dr. Douglas Taylor to the International Conference on Metallurgical Coatings and Thin Films, April 15, 1999. The conference was sponsored by the American Vacuum Society and held in San Diego, California.

Progress on the research supported under this contract was presented at the AFOSR/ONR/ NSF Tribology Program Review by Dr. Douglas J. Taylor on June 15, 1999. The program review was sponsored by AFOSR, ONR and NSF, and was held in Islamorada, Florida.

Dr. Taylor presented a talk entitled "Sol-Gel Derived Nickel Titanate for Tribological Coatings" at the 102nd Annual Meeting of the American Ceramic Society, May 1, 2000. This talk was part of the special symposium on commercialization of sol-gel technology. It was held in St. Louis, Missouri.

A presentation on related work was delivered by Dr. Taylor at the Twelfth Annual Rio Grande Regional Symposium on Advanced Materials, October 16, 2000. The work was entitled "Striation Prevention by Targeted Formulation Adjustment: Aluminum Titanate Sol-Gel Coatings." This work was discovered while investigating aluminum titanate as a tribological coating similar to the primary material under consideration in this contract: nickel titanate. The meeting was held in Albuquerque, New Mexico and was sponsored by the local chapters and sections of ASM International, the American Ceramic Society, and the Materials Research Society.